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AUTOMATIC DETERMINATION OF SULFATES BY AN IMPROVED NEPHELOMETRIC METHOD. APPLICATION TO THE DETERMINATION OF SO2 IN THE AMBIENT AIR AND OF SULFATES IN RAINWATER

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AUTOMATIC DETERMINATION OF SULFATES BY AN IMPROVED NEPHELOMETRIC METHOD

APPLICATION TO THE DETERMINATION OF SO_2 IN THE AMBIENT AIR AND OF SULFATES IN RAINWATER

[Dosage automatique des sulfates par un methode nephelometrique amelioree
Application au dosage du SO_2 dans l'air ambiant et des sulfates dans les eaux de pluie]

By

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An automatic nephelometric method for the determination of low concentrations of sulfate is described. It permits the determination of concentrations as low as 0.1 $\mu g\ cm^{-3}$, The sulfate ions are precipitated by means of barium perchlorate. Fifty samples can be analyzed per hour. This method was developed for the determination of sulfur dioxide in air after absorption in diluted hydrogen peroxide. It is also applicable to the determination of sulfate amounts in rainwater. The equipment used is the Technicon Auto Analyzer connected with a two-monochromator spectrofluorimeter.

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1. Introduction

The hydrogen peroxide method (O.C.D.E., 1964) with acidimetric titration is used for the determination of SO_2 in the samples of the Belgian Network of atmospheric pollution surveillance.

This method, selected by reason of its simplicity, is exposed, however, to interferences due to gases of an acid or alkaline nature. Its application to the determination of samples from industrial or rural areas might therefore yield results that are not truly representative of reality. The selective determination of sulfate ions makes it possible to overcome this drawback by providing an actual value of the quantity of H_2SO_4 formed, and therefore, of the SO_2 content of the atmosphere.

The determination of small quantities of sulfate is, nevertheless, a difficult problem. Most of the known methods use the precipitation reaction with a barium salt.

The turbidimetric methods (Parr and Staley, 1931; Treon and Crutchfield, 1942; Volmer and Frohlich, 1944; Corbett, 1948; Matty and Diehl, 1957; PHS publication No. 999-AP-11), the nephelometric methods (Toennies and Bakay, 1953; Keily and Rogers, 1955), and conductometric titration (Egner, Brodin and Johansson, 1955; O.C.D.E., 1964) have a sensitivity of 1 µg SO_4^{2-} cm^{-3}, which corresponds to about 20 µg SO_2 m^{-3} of air under the experimental conditions that we use. These methods are, however, slow and therefore not very practical if a large number of samples have to be analyzed rapidly.

In addition, the turbidimetric and nephelometric methods require a rigorous control of operating conditions in order to obtain reproducibility and a valid accuracy. The nephelometric titration methods (Wickbold, 1955) and the colorimetric titration methods with Thorin indicator (Fritz and Yamamura, 1955;

O.C.D.E., 1964) are, insofar as they are concerned, very slightly sensitive, their limits of detection being, respectively, 15 and 10 µg SO_4^{2-} cm^{-3}. Contents of the order of 0.3 µg SO_4^{2-} cm^{-3} can be measured thanks to a Thorin colorimetric method automatized by Persson (1966). Another colorimetric method, using barium chloranilate, permits detection of 2 µg SO_4^{2-} cm^{-3} (Bertolacini and Barnes, 1957; Gales, Kaylor and Longbottom, 1968).

Insofar as we are concerned, we studied a sulfate determination method that should be accurate and specific, while being fast, very sensitive and reproducible. We selected nephelometry and we sought to minimize to the utmost the causes of error that generally affect it. We paid particular attention to the factors that affect reproducibility.

2. Experimental Study

2.1. Principle of the method used

The Baird Atomic Fluorispec SF 1 two-monochromator spectrofluorimeter was used as the nephelometer.

When a sample of distilled water is irradiated with a light of wavelength λ_0, a radiation with a wavelength $\lambda_d = \lambda_0$ is obtained in the direction perpendicular to the incident light (Fig. 1). With our spectrofluorimeter, and under the selected operating conditions, the width of the scattering band obtained is about 30 nm.

If the same operation is carried out substituting a suspension of $BaSO_4$ in an ethanol-distilled water medium for distilled water, we obtain a scattering band of a different shape (Fig. 1), though its maximum is still situated in the same wavelength λ_0. A shoulder corresponding to a stronger scattered intensity in the case of the suspension than in the case of distilled water is

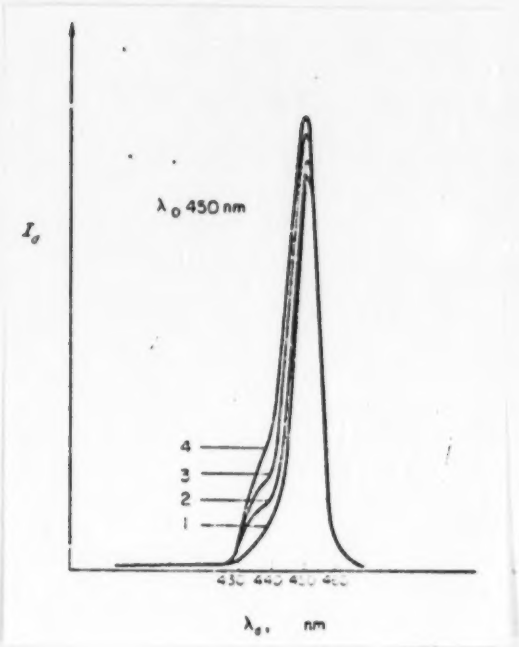

Fig. 1. Intensity of scattered light as a function of wavelength, with (1) distilled water; (2) a solution containing 1.5 µg of sulfate per cm^3; (3) a solution containing 5 µg of sulfate per cm^3; (4) a solution containing 10 µg of sulfate per cm^3.

actually observed there, and this at certain wavelengths shorter than λ_0. This observation was repeated with several λ_0; the phenomenon is more remarkable for λ_0 = 360 and 450 nm; its magnitude increases with the order of the precipitate. The phenomenon is no longer observed for $\lambda_0 > 520$ nm due, no doubt, to the $BaSO_4$ particle size obtained under the experimental conditions that we adopted.

The quantity of $BaSO_4$ in suspension can thus be accurately determined on the basis of the quantity of diffused light, the prudent choice of λ_0 and of the λ_d at which the measurement is made makes it possible to obtain a very good sensitivity. The λ_d of the measurement will be chosen shorter than λ_0,

at the place where the scattered intensity ratio with and without $BaSO_4$ suspension is gratest (Fig. 1).

The choice of suspension medium is also very important. Toennies and Bakay (1953) observed that the quantity of scattered light (I_d) was greater in the ethanol-distilled water medium than in glycerol, and that it depended on the concentration of organic solvent. We decided on ethanol because it provides an appreciable gain in sensitivity.

Dioxane was not adopted, because we planned to use a Technicon autoanalyzer for sample conditioning, this being done for the purpose of having reproducible operating conditions. The use of such a solvent with this equipment is actually difficult; it requires the use of the mercury displacement technique.

2.2. Equipment

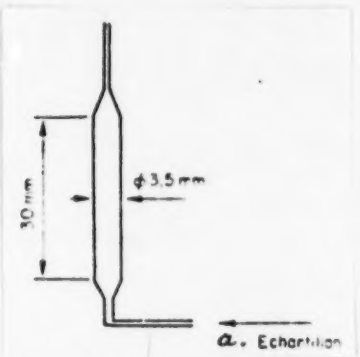

Fig. 2. Optical Measurement cell.

Key: a. Sample

The spectrofluorimeter set to λ_0 = 450 nm and λ_d = 435 nm is equipped with a cylindrical borosilicate-glass cell produced in the laboratory (Fig. 2). This cell permits a continuous flow of liquid, and it can be readily connected to a Technicon autoanalyzer unit whose ultimate form is shown (Fig. 3). The quantities of reagents added, the mixture thereof and the reaction time prior to measurement can be rigorously standardized thanks to this equipment. Control of these factors is actually very important if accurate and reproducible results are to be obtained. They have a strong influence on the form of the precipitate, on particle size, etc.

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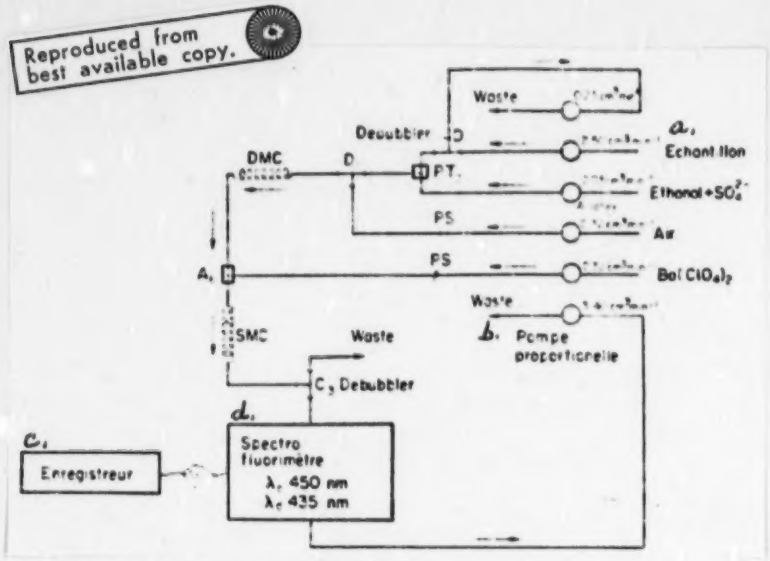

SMC: Simple mixing coil
DMC: Double mixing coil
PS: Pulse suppressor

Fig. 3. Diagram of the manifold used for the Technicon Auto-Analyzer

Key: a. Sample; b. Proportional pump; c. Recorder; d. Spectrofluorimeter.

Acidflex quality tubes are preferred over Solvaflex for the addition of ethanol, though the Solvaflex are recommended by Technicon for contents ranging up to 40% ethanol. Small amounts of Solvaflex tubes are dissolved during the punping of 40% ethanol solutions. The dissolved materials precipitate again in the form of very fine particles at the time of the sample/ethanol solution mixture, and this hampers measurement. The alcohol content actually drops to 15-20% after this mixture.

The introduction of the sample in the manifold is done thanks to a very very fast circular sampler constructed in the laboratory and operating with compressed air. Passage from one sample to the next should actually be done in a few tenths of a second so as not to introduce too large quantities of air

into the analysis system, since they might be the cause of substantial disturbance due to variations in the ethanol/distilled water ratio in the mixture. These variations cause variations in density in the $BaSO_4$ suspension liquid; the measurement cell is therefore the site of substantial turbulences, which is the cause of great signal instability.

The sampler is provided with cups of about 4 cm^3 that alternately contain the samples and the distilled water intended for washing the circuit between each analysis, the sample suction time being two times longer than that of the blank.

This assembly makes it possible to analyze 48 samples per hour without risk of contamination.

The small air bubbles that enter into the system during passage between two samples are removed at Debubbler D1 (Fig. 3). The addition of ethanol to the sample takes place at PT2, and this mixture is broken up by air bubbles at D1. The path of the sample up to the point of fragmentation must also be as short as possible in order to prevent, insofar as possible, the interference of one sample with its neighbors. Double coil DMC provides for proper homogenization of the mixture to which the $Ba(ClO_4)_2$ solution is added immediately thanks to an A6-type T-shaped element. The $BaSO_4$ precipitate is thus formed and kept in suspension thanks to a simple coil SMC. Following passage through debubbler C3, this suspension is pumped again through the optical measurement cell from the bottom upwards.

2.3. Reagents

2.3.1. Standard sulfate solutions. Standard solutions containing from 0.15 to 150 µg SO_4^{2-} cm^{-3} can be obtained from 0.1 N H_2SO_4 by preparing suitable

dilutions by means of distilled water or a absorbent reagent used for SO_2 determination (0.3% perhydrol).

2.3.2. Barium perchlorate solution. Four to 5 g of $BaClO_4)_2$ are dissolved in 250 cm^3 of distilled water; 1.5 cm^3 of 70% $HClO_4$ are then added to the solution obtained.

2.3.3. Alcohol solution. Per liter of solution: 400 cm^3 of ethanol (denatured ethanol may be suitable); 20 cm^3 of a sulfate solution containing 30 µg SO_4^{2-} cm^{-3}; 580 cm^3 distilled water.

2.4. Discussion of the different parameters -- Optimal research conditions

The effect of the different parameters was the object of careful study in order to optimize operating conditions.

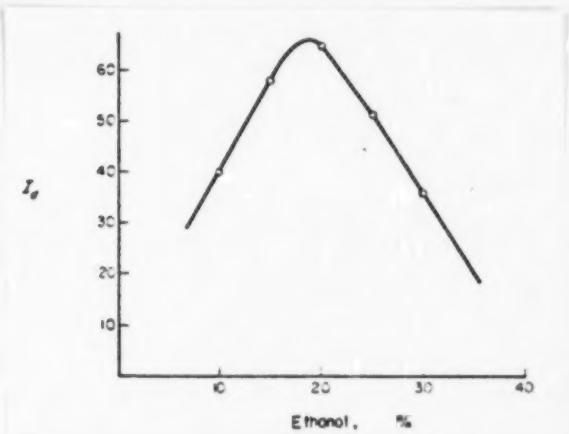

Fig. 4. Scattered intensity as a function of percentage of ethanol in the solution.

2.4.1. Ethanol concentration. The effect of the ethanol content in the sample on sensitivity is shown (Fig. 4). Optimum sensitivity is obtained with 15-20% ethanol in the analysis medium.

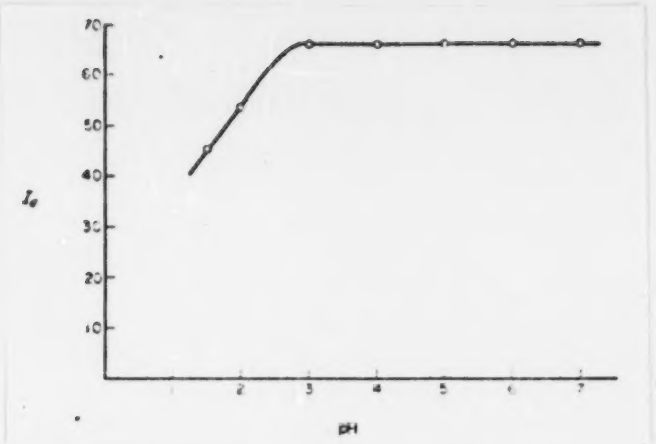

Fig. 5. Scattered intensity as a function of the pH of the solution.

2.4.2. Acidity. Fig. 5 clearly shows that the intensity of the scattered light is constant and maximal for pH values ranging from 3 to 7.

2.4.3. $Ba(ClO_4)_2$ solution. The $Ba(ClO_4)_2$ solution has a remarkable effect on the sensitivity of the method. The best results were obtained with the solution as described in 2.3.2; it contains an appreciable excess of Ba^{2+} ions.

The age of the solution is an important element to be taken into consideration. It is preferable, if stable sensitivity is desired, to allow it to age for one hour prior to use. Its use, after it has aged more than nine hours, should be avoided. These conditions of use are prescribed by experience; it is actually very difficult to evaluate them theoretically.

The addition of a quantity of ethanol corresponding to 20% makes it possible to increase sensitivity. The density of the $Ba(ClO_4)_2$ solution is thus of the same order as that of the sample-ethanol mixture; the formation of density gradients and turbulence at the time of $BaSO_4$ precipitation are thus avoided.

2.4.4. Sample conditioning (Technicon Autoanalyzer). Proper operation of the unit depends for the most part on the manner in which the sample-ethanol mixture is prepared. The mixture actually presents certain difficulties owing to the difference in density of these two components. The mixture should be made and homogenized very rapidly so that the measurement cell is not the site of any turbulence due to a density gradient. The manifold and the shape of the optical cell are designed as a function of these requirements. The manifold, schematically shown in Fig. 3, responds to these requirements perfectly.

Other configurations were tested with less success, especially:

(a) The use of a $Ba(ClO_4)_2$ solution in a water-ethanol medium, and successive additions of: 150 µg SO_4^{2-} cm^{-3} solution; sample.
Passage through the optical cell following a double mixing coil.

(b) Successive additions to the sample of: aqueous solution of $Ba(ClO_4)_2$; ethanol-water mixture (40-60) with 150 µg SO_4^{2-} cm^{-3} solution.
Passage through the optical cell following a double mixing coil.

2.4.5. Study of interferences

(a) Presence of KCl. The intensity of scattered light is 10% greater if the sample contains KCl. This may be due to the increase of the ionic force of the medium, which affects the shape of the particles of the $BaSO_4$ precipitate.

(b) Presence of nitrates, phosphates, Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+} ions. There is no significance effect up to contents of the order of 200 µg cm^{-3} of these ions.

2.5. Analytical performances

2.5.1. Limit of detection. Toennies and Bakay (1953) stressed the difficulty of $BaSO_4$ precipitation with low sulfate contents (less than 0.6 mg l^{-1});

the formation of the precipitate is actually slow and uncertain there.

This obstacle was overcome by adding a small known quantity of SO_4^{2-} ions to the sample. We are thus situated in an area of concentrations where precipitation is certain and quick.

This addition is carried out, in practice, in the ethanol-water mixture during sample conditioning. It is thus constant and identical for all samples, both for the standard solutions and for the "blanks."

Proceeding in this manner, it is possible to measure contents as low as 0.1 mg SO_4^{2-} l^{-1}, which corresponds to about 1.7 µg SO_2 m^{-3} of air for 50 cm^3 samples through which about 2 m^3 of air are passed.

2.5.2. Area of application. We have applied the method to samples containing up to 150 mg SO_4^{2-} l^{-1} without encountering any special problem. The calibration curve was still a straight line in this case. We did not test higher concentrations, since as the $BaSO_4$ precipitate was very substantial there it might adhere partially to the walls of the optical cell and of the manifold tubes thus impairing the analysis of the following samples when the particles leave the walls to which they have adhered.

Moreover, 150 mg SO_4^{2-} l^{-1} was already, in our case, substantially higher than what we would normally find; it actually corresponds to about 2.550 µg SO_2 m^{-3} of air.

2.5.3. Accuracy of results. The error of the results depend on the area of concentrations in which they are situated. If the standardization of the analytical chain is carried out regularly (about every hour), the relative error is small, as shown in Table 1.

Table 1

Relative Errors

Concentrations in SO_4^{2-} (mg l^{-1})	Relative error (%)
1.5	2.88
3.0	1.76
6.0	1.55
9.0	0.95
12.0	0.67
15.0	0.66
75.0	0.61
150.0	0.59

3. Practical Observations

The analysis of the samples from the "Sulfur-Smoke" apparatus, where the absorption of SO_2 is made in a perhydrol solution, is possible without any prior treatment. About 4 cm^3 of these samples can therefore be placed directly in the cups of the sampler. Fig. 6 shows the diagram obtained with a series of samples.

Rainwater analysis affords no difficulty; in this case it is preferable to add KCl to the alcohol solution (2.3.3), at the rate of 100 cm^3 of saturated KCl per liter of solution. This is useful in order to eliminate the effect of the ionic force of the medium and to increase sensitivity. The 4 cm^3 of rainwater intended for analysis will be taken as high as possible from the mass of water collected in order to avoid the presence of solid particles in the sample. If the quantity of precipitation is too small and does not permit such a guarantee, it is desirable to filter or centrifuge the sample.

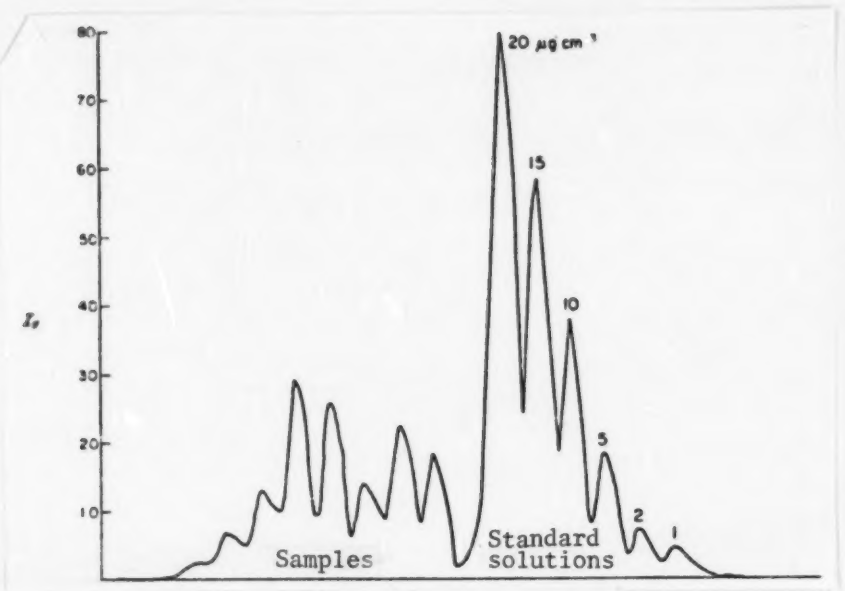

Fig. 6. Diagram obtained with a series of standardization and samples.

The optical cell and the mixing coils must be washed with concentrated H_2SO_4 and carefully rinsed every 2,000 samples. The very fine particles that might accumulate there over a period of time causing a loss of sensitivity and a lack of stability of the base line can thus be readily removed.

4. Conclusions

Automation of nephelometry, thanks to an Autoanalyzer, and use in a two-monochromator spectrofluorimiter employed as a nephelometer have permitted the very specific and precise determination of sulfates, even in small quantities. The advantage of the method described is derived to a large extent from the fact that the standard solutions and the samples are treated in the same manner and in a very reproducible form.

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